

# Cause of the chalcophile trace element enrichments marking the Holocene to Anthropocene transition in northern Chesapeake Bay sediments

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## Abstract

In Chesapeake Bay sediments, concentrations of 15 chalcophile trace elements, half rarely determined in estuaries, display historical profiles having remarkably similar features. All element concentrations rose more or less simultaneously in the 1920–1940 interval, creating a chemostratigraphic marker of the Holocene to Anthropocene transition. Subsequently, concentration maxima occurred at ~20-year intervals, suggesting a link to a documented climate cycle of similar period. These elements' correlated profiles suggest that sediments approximate binary mixtures of one lithogenic and one multi-element anthropogenic component. The latter component is characterized by these mass ratios ( $\pm$ standard error):

Co/Zn $0.071 \pm 0.003$	Cu/Zn $0.147 \pm 0.007$	Ag/Zn $0.0030 \pm 0.0002$
Cd/Zn $0.0050 \pm 0.0004$	In/Zn $0.00031 \pm 0.00004$	Sn/Zn $0.019 \pm 0.002$
Sb/Zn $0.0040 \pm 0.0002$	Te/Zn $0.00059 \pm 0.00003$	Tl/Zn $0.0016 \pm 0.0002$
Pb/Zn $0.242 \pm 0.013$	Bi/Zn $0.00087 \pm 0.00005$	

Where comparisons are possible, these ratios differ from those of contaminants in the harbor of the region's principal industrial city, Baltimore, but are surprisingly similar to those in sediment contaminants from the Susquehanna River, the Bay's chief tributary. Thus both the anthropogenic and the lithogenic components in the Bay's central channel appear to originate in the river basin. Many chalcophile element ratios in the anthropogenic component are similar to those in regional aerosols. If cumulative aerosol deposition on soils in the river basin is the source of the anthropogenic component, then the above ratios could be a regional anthropogenic signature that should be looked for more widely. Unlike Mo, the enrichment of these chalcophile elements in the Bay's sediments is not controlled by seasonal anoxia; Mo apparently possesses a unique capacity to record past redox information about estuaries owing to its high seawater concentration.

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## 1. INTRODUCTION

Oxygen-starved, often sulfidic dead zones in estuaries and coastal marine waters are globally expanding threats to mar-

ine ecosystems, including fisheries (Diaz and Rosenberg, 2008). Dead zones are attributed to fixed nitrogen and phosphorus pollution, which causes eutrophication. Chesapeake Bay, on the mid-Atlantic Coast of the United States, is one of the localities where this problem was first described (Newcombe and Horne, 1938; Taft et al., 1980; Officer et al., 1984a; Seliger et al., 1985), and it remains one of the most intensively studied examples (Hagy et al., 2004; Kemp et al., 2005; Gooday et al., 2009). In a typical recent year in the northern half of this estuary, water below 10 m depth is

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severely O<sub>2</sub>-depleted from June to September; sulfide is often observed, but generally does not exceed 10 μM (Lewis et al., 2007).

Seasonal anoxia began in Chesapeake Bay before environmental monitoring was routinely performed, so circumstances leading to its onset were initially unclear. Adelson et al. (2001) showed that Mo enrichments in dated sediments from the Bay's central, deep channel appeared to preserve a useful record of anoxia's history. Such records, produced by both geochemical and paleontological methods, are invaluable for environmental management, so methods for generating them are currently the focus of active research (Gooday et al., 2009). It is of interest to enquire what information about past redox conditions might be accessible from other trace elements.

Research on trace elements as paleoproductivity and paleoredox indicators has largely been undertaken at marine sites remote from human influence (see reviews by Brumsack, 2006; Calvert and Pedersen, 2007). Employing these approaches to reconstruct environmental history in anthropogenically impacted coastal waters can be frustrated by two potentially serious difficulties. The first is that sediment accumulation rates in estuaries and coastal waters are often ~10<sup>3</sup> greater than in the ocean. Only very strong signals from productivity- or redox-linked processes will be readable against dilution at estuarine sedimentation rates. The second is that industrial pollution might easily overprint subtler authigenic signals caused by environmental redox changes. Adelson et al. (2001) presented evidence that industrial sources of Mo could be neglected in Chesapeake Bay, a result now reinforced by Mo isotope measurements (Scheiderich et al., 2010). On the other hand, Adelson et al. noted that Cu profiles in sediments appeared to be dominated by industrial activities and would therefore preserve little redox or productivity information.

Prior studies of chalcophile trace elements in Chesapeake Bay sediments have been regionally extensive, but limited to only a few elements. The earliest surveys of trace elements in Chesapeake Bay sediments, undertaken about 30 years ago, showed that the entire, 300 km main channel (but especially the northern half) was pervasively enriched with Zn and Pb relative to preindustrial sediments and to shales (Helz, 1976; Sinex and Helz, 1981; Helz et al., 1985a; Rule, 1986). Enrichment of other first-row transition metals also occurred, but was less pervasive. Several groups subsequently have contributed important additional trace element information (Owens and Cornwell, 1995; Zimmerman and Canuel, 2000, 2002; Marcantonio et al., 2002; Zheng et al., 2003).

For a site about 50 km southeast of Baltimore, the principal industrial center on northern Chesapeake Bay, we recently described readily measureable enrichments relative to preindustrial sediments and shales of a larger group of chalcophile trace elements than has been studied previously (Dolor et al., 2009). The defining characteristic of chalcophile elements, their strong reactivities toward sulfur, makes them candidates to record historical information about redox conditions. In this paper, we explore causes of enrichment of these elements at that site.

## 2. METHODS

The Chesapeake Bay sediment samples come from two archived sediment cores (see location map, Fig. 1). Data from the cores were spliced to obtain a record spanning the 20th century. Because age uncertainty increases with depth in cores, older samples usually are dated less accurately in a single core than is possible in spliced cores that were collected several decades apart. However, there will always be some risk that splicing generates artifacts, as discussed later.

Core 55 was collected in July 1979 and Core RD was collected in November 1998. Both are from the central channel of Chesapeake Bay and were collected from sites less than 10 km apart. The water depth at these sites (25 m and 26.5 m, respectively) is substantially below the pycnocline (~10 m), so both sites have been overlain by O<sub>2</sub>-depleted water during summers. Owing to O<sub>2</sub> stress, sediments are minimally disturbed by burrowing organisms. Additionally, we will discuss several samples from a Susquehanna River core collected from the reservoir above the Conowingo Dam in May, 1979. Conowingo Dam (finished in 1928) is the most southerly of three dams on the lower Susquehanna River.

Mass accumulation rates have been published previously for all three cores primarily based on the <sup>210</sup>Pb dating method, but with verification by <sup>137</sup>Cs and <sup>239,240</sup>Pu, as well as other date markers (Officer et al., 1984b; Helz et al., 1985b; Zimmerman and Canuel, 2002). The rates are: Core RD 1.21 g/cm<sup>2</sup>/y; Core 55 0.41 g/cm<sup>2</sup>/y; Susquehanna 2.88 g/cm<sup>2</sup>/y. Near-bottom tidal currents create the differences in mass accumulation rates displayed by cores RD and 55.

All elements except Mn were determined simultaneously by laser ablation ICP-MS, as detailed in our recent paper (Dolor et al., 2009). Manganese was chosen as an internal standard for workup of the LA-ICPMS data because it tends to occur in grain coatings, rather than in specific mineral grains, and is therefore likely to be more uniformly distributed. It was determined in nitric-hydrofluoric acid digestates of the sediment samples by ICP-MS (Dolor et al., 2009). Sediment samples for laser ablation were prepared simply by pressing them into pellets without adding a binder or other extraneous material. The samples consisted predominantly of clay-sized (<4 μm) particles, so each laser shot with the 100 μm beam ablated hundreds or thousands of such particles. An analysis consisted of 150 laser shots in a 1.5 mm track across a pellet, and each such analysis was replicated four times per pellet. Calibration was with geochemical standards, primarily the fine-grained marine sediment, MAG-1.

The analytical precision is illustrated in Fig. 2 based on repeated analyses during a period of several weeks of two geochemical standards, MAG-1 and SCo-1 (Schultz et al., 1976). In most cases, the precision is better than ±10%; only in the case of Cd in MAG-1 was the precision worse than ±20%. Random variations that degrade precision are not necessarily due entirely to the analytical procedure; some may arise from sample inhomogeneity. Slightly greater inhomogeneity might explain the moderately poorer

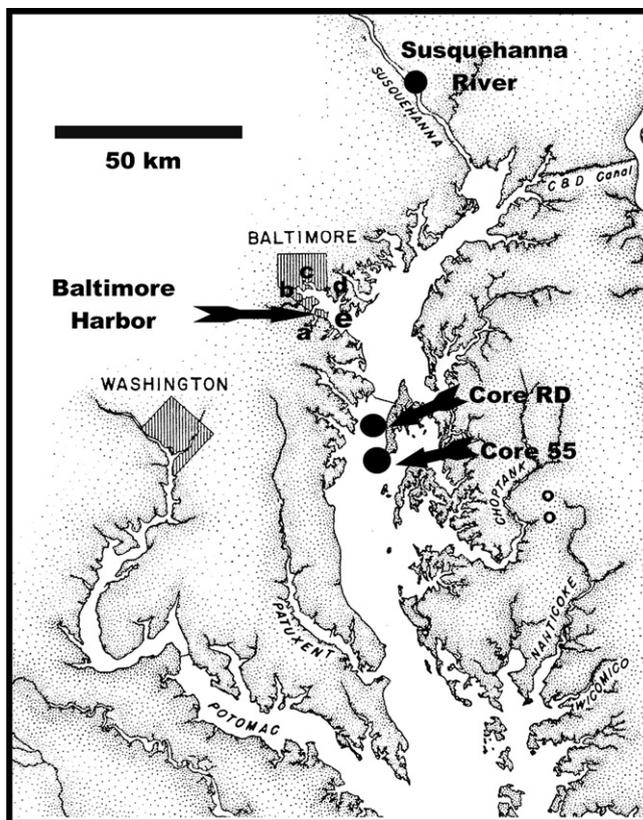


Fig. 1. Map of northern Chesapeake Bay showing sample localities. Site marked Susquehanna River lies within the Conowingo Reservoir. Lower case letters around Baltimore Harbor designate tributaries: (a) Curtis Bay, (b) Middle Branch, (c) Northwest Branch (also known as the Inner Harbor), (d) Bear Creek and (e) Outer Harbor.

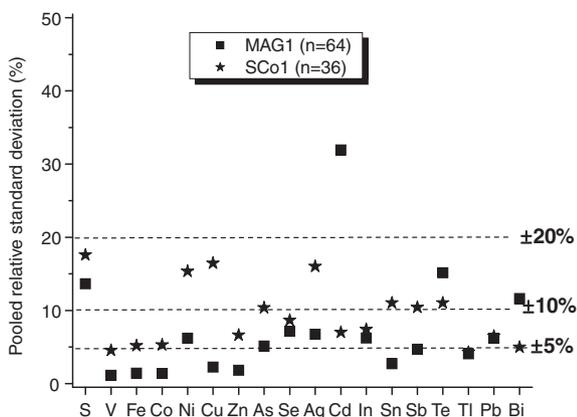


Fig. 2. Analytical reproducibility for two geochemical standards, a marine mud powder from the Gulf of Maine (MAG1) and Cody Shale powder from Wyoming (SCo1).

reproducibility obtained in Fig. 2 with SCo-1 compared to MAG-1. Results from this LA-ICP-MS method were demonstrated (Dolor et al., 2009) to agree well with previously published analyses of these same samples by independent, single-element methods such as DC plasma emission spectroscopy and atomic absorption spectroscopy (Cantillo et al., 1984; Adelson et al., 2001; Marcantonio et al.,

2002). This demonstration affirmed the validity of the analytical approach, including the choice of Mn as the internal standard. Additional details about methods as well as data tables are provided elsewhere (Dolor, 2009; Dolor et al., 2009).

### 3. RESULTS

In Fig. 3, we present data for the most abundant components quantified,  $C_{org}$ , S, Mn and Fe. Where samples from the two cores overlap in age, concentrations of these components (as well as the trace elements described below) are in reasonable agreement. It therefore seems acceptable to splice them, as done in this figure.

The carbon and sulfur contents are high relative to average shale. Sulfur shows proportionately the greatest vertical concentration variation (4-fold max/min range) but no systematic trend with time. This variation reflects sulfur's introduction to the sediments primarily by diagenetic processes that vary from year to year. Previously determined ratios of acid volatile to chromium reducible sulfur in Core RD (Zimmerman, 2000; Zimmerman and Canuel, 2002) also vary considerably, although AVS always exceeds 1 mg/g.

Ample reactive sulfide, in the form of AVS, will tend to suppress post-depositional mobility of most chalcophile trace elements (DiToro et al., 1992; Cooper and Morse,

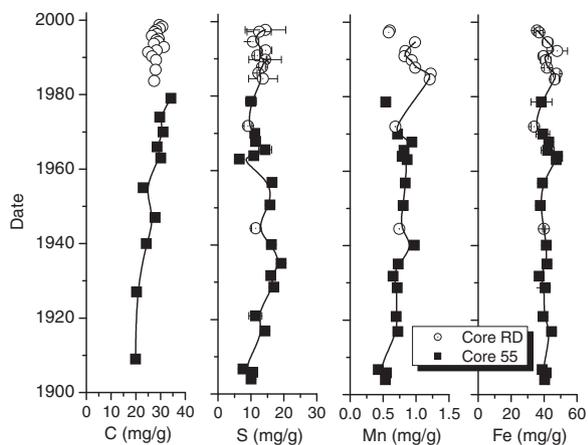


Fig. 3. Most abundant components determined in Cores RD and 55. Organic carbon from Cantillo (1981) and Zimmerman (2000). Sulfur and iron determined by LA-ICPMS; error bars are standard deviations ( $1\sigma$ ) calculated from four replicate determinations. Manganese was determined by ICPMS on acid extracts of sediments. Concentrations (dry weight basis) have been plotted vs. date of deposition as calculated from mass accumulation rates.

1998). However, exceptions are elements like As, which form relatively soluble sulfide minerals in neutral-to-alkaline solutions (Helz and Tossell, 2008). (Pore water pH in the Bay's central channel is about 7.5; Matisoff et al., 1975.) For example, As is observed to escape from sediments that underlie anoxic waters in the Bay, while Cu and Cd are retained (Riedel et al., 1999).

Iron concentrations are similar to average shale and show proportionally the least vertical variation (1.4-fold max/min range). Except for possible weak concentration peaks in the 1960s and 1980s (discussed below), Fe concentrations did not change appreciably over the entire 20th century. This indicates that sources supplying sediment to the deep channel have been stable.

Manganese is more variable (2.8-fold max/min range) vertically than Fe, but much less variable than many of the trace elements to be discussed below. Note that the top sample in Core 55 and the top two samples in Core RD seem distinctly depleted in Mn relative to samples below them. This probably reflects well-known reductive dissolution of Mn oxyhydroxides in near-surface sediments and precipitation of downward diffusing  $Mn^{2+}$  as a carbonate at greater depth (Holdren et al., 1975). Owing to this process, sediments acquire their final Mn concentrations only after burial to several centimeters. Sulfur, which is also acquired by the sediment mainly through diagenetic processes, does not display similar surface depletion.

Fig. 4 shows data for 15 chalcophile trace elements. Data points are means obtained from four laser tracks on each sample pellet. Error bars depict pooled standard deviations (Skoog et al., 2000), based on individual standard deviations for each track. To differing degrees, profiles for all elements exhibit two interesting features: first, a systematic concentration increase during approximately the 1920–1940 period, and second, some striking concentration peaks, located roughly in the mid-1960s and mid-1980s (e.g., note especially Co, Ag, Pb profiles). In some of the

element profiles, a third peak is discernable near 1940 (e.g., Se, Sn, Pb). In several cases (Zn, Ag, Pb and Bi), post-1940 concentrations are extraordinary, even exceeding average concentrations at classic metalliferous sediment localities like the Black Sea (Brumsack, 2006).

Commonly, trace metal concentrations in modern estuarine sediments are viewed as composed of two components. One is a background or lithogenic component generated by natural weathering and erosion. The other is an excess component, usually attributed to human activities or to authigenic mineral formation. The concentration of an element in this latter component,  $M_{ex}$ , is conventionally calculated as follows:

$$M_{ex} = M_{obs} - Fe_{obs}(M_{litho}/Fe_{litho}) \quad (1)$$

Here,  $M_{obs}$  and  $Fe_{obs}$  are the measured concentrations of element M and Fe, respectively;  $M_{litho}$  and  $Fe_{litho}$  are the corresponding concentrations in the lithogenic component. We take the average M/Fe ratios in samples deposited before 1910 in Core 55 as an estimate of  $M_{litho}/Fe_{litho}$ . These values are similar to those in median shale (Dolor et al., 2009).

Some authors prefer to use Al, rather than Fe, as the normalizing element, but in rapidly depositing coastal and estuarine sediments either can be used with equivalent results (Daskalakis and O'Connor, 1995). We use Fe of necessity because to optimize our analytical protocol for as many chalcophile trace elements as possible, we had to abandon Al determinations.

With the exceptions of  $Ni_{ex}$ ,  $As_{ex}$  and to a lesser extent  $Se_{ex}$ , most  $M_{ex}$  concentrations are well correlated with each other, as shown in Table 1. We have highlighted in bold type the table's correlation coefficients that have less than a 2% probability of arising in uncorrelated data. Although arbitrary, the 2% level of significance turns out to be a convenient boundary. As the table shows, correlations of  $Ni_{ex}$ ,  $As_{ex}$  and  $Se_{ex}$  with the other elements are mostly insignificant at this level, whereas all the others correlate significantly. In the remainder of this paper, we make use of this boundary to define two chalcophile element classes, which we call uncorrelated elements ( $Ni_{ex}$ ,  $As_{ex}$  and  $Se_{ex}$ ) and correlated elements (all the others). We will argue that correlations among the latter class arise because excess concentrations of these elements originate from the same dominant source or process.

Fig. 5 illustrates relationships among excess concentrations of chalcophile elements graphically. We chose  $Zn_{ex}$  for the horizontal axis in this figure simply because it is the most abundant and among the most precisely measured of the correlated chalcophile trace elements. In this figure,  $Ni_{ex}$ ,  $As_{ex}$  and  $Se_{ex}$  are seen to have numerous negative values. Apparently the reason that these elements are uncorrelated with the others is that their excess concentrations are small in relation to sources of variance, including but not restricted to analytical error.

The regression lines in Fig. 5 can be viewed as statistical estimates of mixing lines. They connect the lithogenic component, which plots at the origin (all  $M_{ex} = 0$ ), to a hypothesized single excess component, located somewhere along the lines to the upper right. Fig. 5 does not permit locating

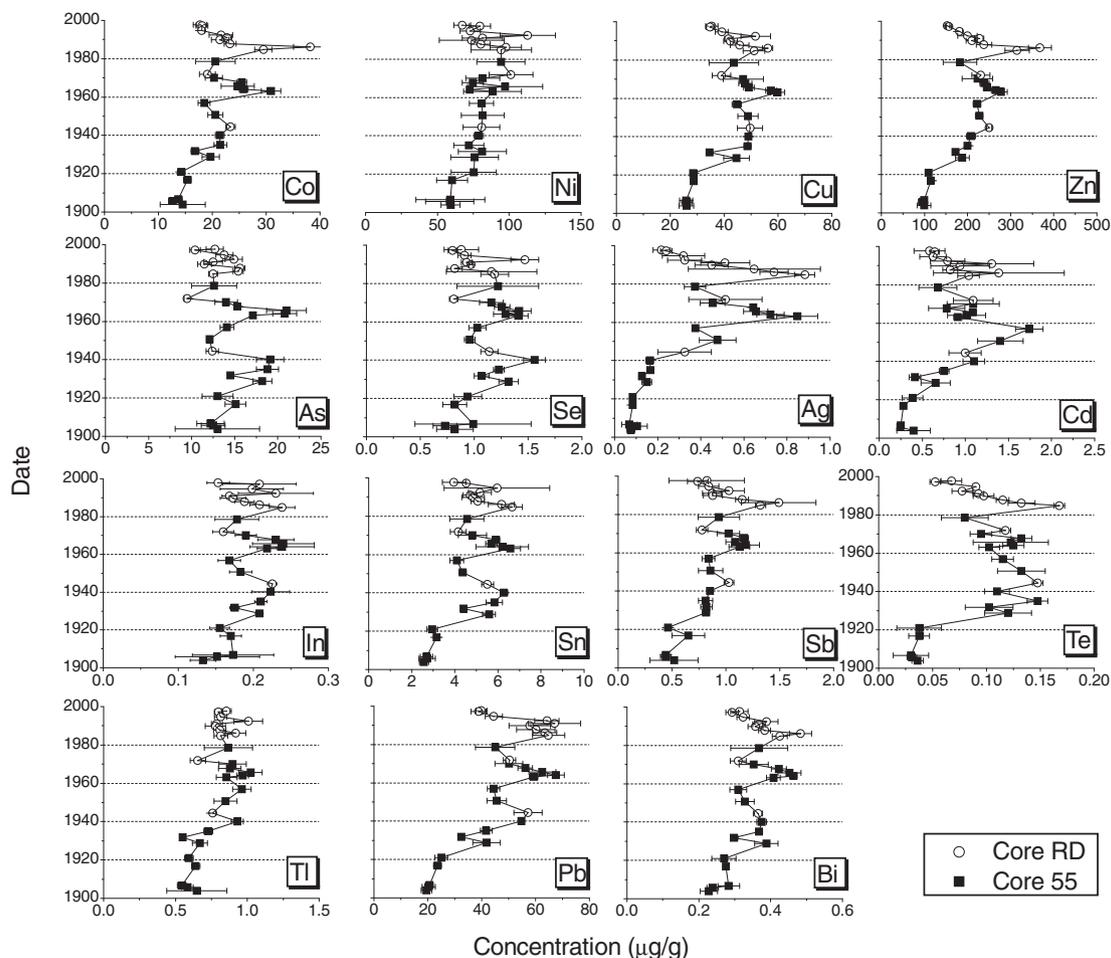


Fig. 4. Concentrations of trace elements in samples vs. date of sample deposition. Data points depict averages of four concentrations obtained from replicate laser tracks. Error bars depict pooled standard deviations ( $1\sigma$ ) computed from the standard deviations for each track.

Table 1

Pearson's product moment correlation coefficients between  $M_{ex}$  concentrations for 15 chalcophile elements in cores RD/55. Bold face indicates cases where the probability that the two elements are not correlated is  $<2\%$  ( $n = 28$ ).

	Co	Ni	Cu	Zn	As	Se	Ag	Cd	In	Sn	Sb	Te	Tl	Pb	Bi
Co	<b>1.00</b>														
Ni	0.22	<b>1.00</b>													
Cu	<b>0.81</b>	0.24	<b>1.00</b>												
Zn	<b>0.94</b>	0.28	<b>0.87</b>	<b>1.00</b>											
As	0.11	-0.18	0.34	0.10	<b>1.00</b>										
Se	0.37	0.23	<b>0.64</b>	0.36	<b>0.60</b>	<b>1.00</b>									
Ag	<b>0.83</b>	0.18	<b>0.72</b>	<b>0.86</b>	0.00	0.17	<b>1.00</b>								
Cd	<b>0.63</b>	0.36	<b>0.74</b>	<b>0.78</b>	0.09	0.30	<b>0.60</b>	<b>1.00</b>							
In	<b>0.49</b>	0.11	<b>0.67</b>	<b>0.54</b>	0.38	<b>0.66</b>	0.39	0.33	<b>1.00</b>						
Sn	<b>0.68</b>	0.12	<b>0.75</b>	<b>0.69</b>	0.27	<b>0.49</b>	<b>0.54</b>	<b>0.44</b>	<b>0.83</b>	<b>1.00</b>					
Sb	<b>0.86</b>	0.21	<b>0.84</b>	<b>0.88</b>	0.27	<b>0.53</b>	<b>0.72</b>	<b>0.62</b>	<b>0.63</b>	<b>0.74</b>	<b>1.00</b>				
Te	<b>0.72</b>	0.21	<b>0.83</b>	<b>0.85</b>	0.29	<b>0.46</b>	<b>0.62</b>	<b>0.68</b>	<b>0.66</b>	<b>0.68</b>	<b>0.75</b>	<b>1.00</b>			
Tl	<b>0.44</b>	0.37	<b>0.66</b>	<b>0.51</b>	0.25	<b>0.46</b>	<b>0.45</b>	<b>0.71</b>	<b>0.46</b>	<b>0.50</b>	<b>0.61</b>	0.41	<b>1.00</b>		
Pb	<b>0.79</b>	0.28	<b>0.86</b>	<b>0.86</b>	0.15	<b>0.44</b>	<b>0.80</b>	<b>0.71</b>	<b>0.60</b>	<b>0.70</b>	<b>0.84</b>	<b>0.73</b>	<b>0.66</b>	<b>1.00</b>	
Bi	<b>0.84</b>	0.19	<b>0.86</b>	<b>0.85</b>	0.41	<b>0.61</b>	<b>0.73</b>	<b>0.59</b>	<b>0.70</b>	<b>0.72</b>	<b>0.85</b>	<b>0.78</b>	<b>0.59</b>	<b>0.86</b>	<b>1.00</b>

the excess component's actual composition, but the slopes of the regression lines define ratios between its chalcophile

trace elements. Thus these slopes are important and will be used as signatures of the excess component.

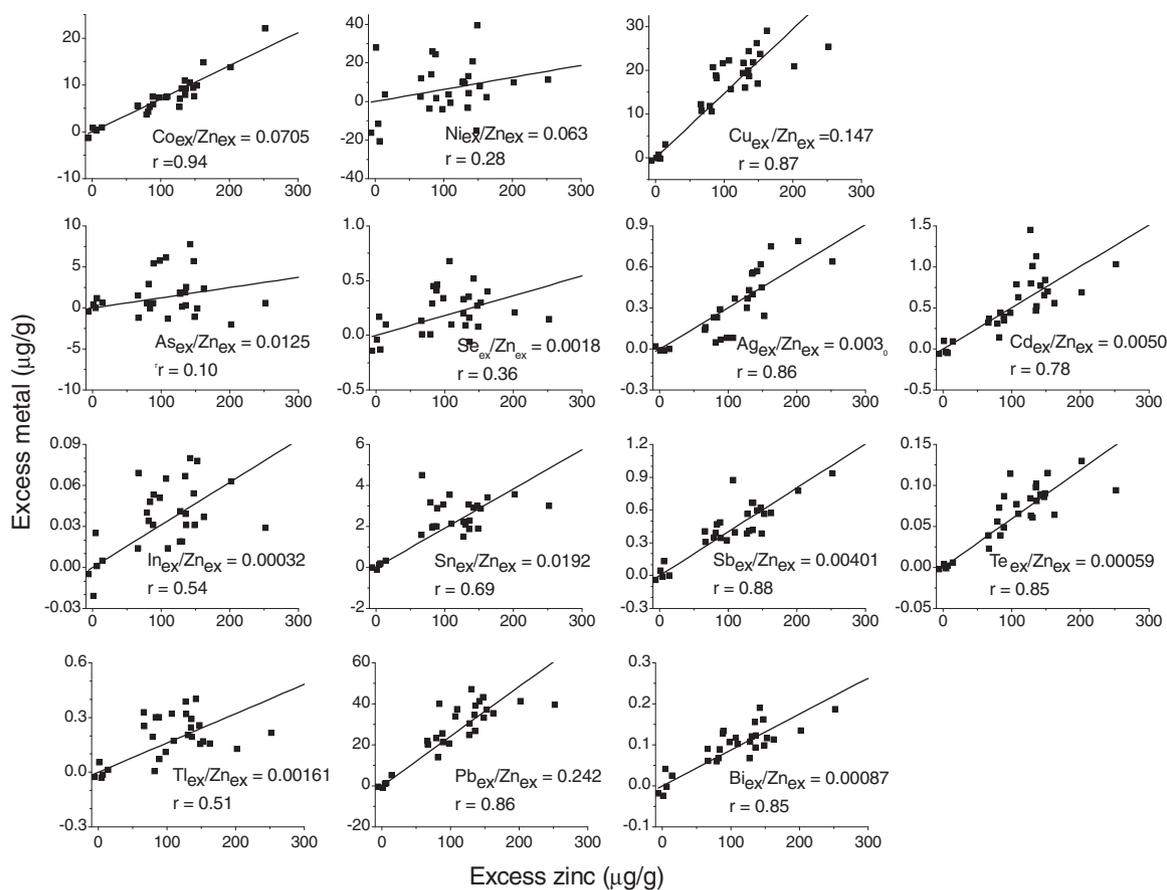


Fig. 5. Correlation of  $M_{ex}$  vs.  $Zn_{ex}$  for fourteen trace elements. See Eq. (1) in text for definition of  $M_{ex}$ . Lines are linear regressions forced through [0,0]. Captions give  $M_{ex}/Zn_{ex}$  mass ratios based on slopes of these lines. For 28 data points, the probability of obtaining  $r \geq 0.44$  in uncorrelated normally distributed variables is less than 2%. At this level, eleven of the fourteen chalcophile metals correlate significantly with  $Zn_{ex}$ .

Differences in peak amplitudes between the various elements in Fig. 4 can be explained by the extent of concentration differences between the lithogenic component and the excess component. An element whose concentration is identical in both components would exhibit no variation in binary mixtures. Iron, which has very muted peaks (Fig. 3), is an element which approaches this limit. At the opposite extreme, the massive peaks displayed by Ag imply a large enrichment of this element in the excess vs. the lithogenic component. Relative to crustal abundance, Ag indeed is the most highly enriched of the elements studied here (Dolor et al., 2009).

The left-hand panel of Fig. 6 gives information about Susquehanna River water discharges during the 20th century. The data points depict average monthly discharges during the five high-flow months (January–May) in each year. Discharges during these months largely control density stratification and thus deep-water ventilation in the Bay during the summer. The curve shows three-year smoothing of the data, highlighting multi-year discharge excursions.

In the right-hand panel of Fig. 6, normalized excess concentrations of the eight most highly correlated chalcophile elements are plotted vs. deposition date. The normalization

method is one commonly used in factor analysis and places the data for all elements on a common, unitless scale. Normalization involves first calculating the means and standard deviations for the excess concentrations of each element in the 1940–2000 time interval. Then the differences between each  $M_{ex}$  value and the mean are taken, and the resulting differences are divided by the standard deviations.

This normalization process highlights evidence of at least two and possibly three concentration peaks. The similarity among profiles for excess concentrations of all elements is consistent with their incorporation into a single, multi-element excess component that is being mixed with the lithogenic component in proportions that vary over time. Most importantly, comparison of the two panels suggests that each concentration peak is associated with a multi-year *minimum* in spring discharge from the river basin.

#### 4. DISCUSSION

These results demonstrate that a broad group of chalcophile elements appear to rise in concentration more or less simultaneously, first becoming measurable in the early 20th century. We know of no natural climatic, hydrologic or geologic events that could account for this phenomenon.

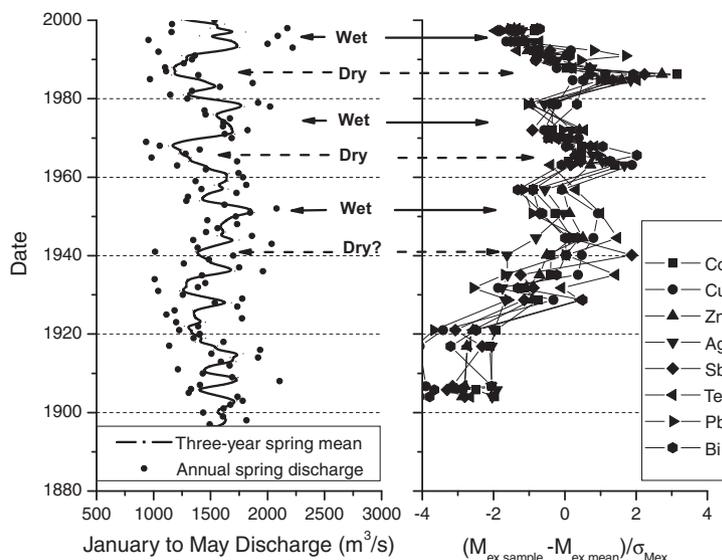


Fig. 6. Left panel: Susquehanna River mean monthly discharge at Harrisburg, PA, during the high-flow, January–May period; points indicate each year's mean monthly January–May discharge and the curve indicates mean monthly discharge after 3-year smoothing (data from the US Geological Survey). The Susquehanna River delivers 90% of the freshwater and most of the sediment entering the Bay north of the Potomac River. Right panel: Normalized excess concentrations of those chalcophile elements that display the greatest correlation with  $Zn_{ex}$ .

Therefore we attribute it to human activities and suggest that it is appropriately described as a stratigraphic marker of the Holocene to Anthropocene transition. Anthropocene is a term proposed by Crutzen (2002) for the current, human-dominated period in Earth history.

The enlargement of trace element concentrations in the early 20th century has been noted previously in Chesapeake Bay (Helz et al., 1985b; Owens and Cornwell, 1995; Marcantonio et al., 2002). However this is the first time that it has been shown to occur at about the same time for such a large group of trace elements in Chesapeake Bay.

Curiously and significantly, this group includes elements that during much of the 20th century had quite different principal anthropogenic sources. For example, the principal anthropogenic Ag sources have been dispersed, small photographic and electroplating activities and discharge has been mainly via wastewater treatment plants. In contrast, the principal Pb source has been gasoline combustion products discharged via the atmosphere. Similarly, this group includes elements with quite different predominant speciation in natural waters (e.g.,  $Tl^+$  vs.  $Sb(OH)_5^-$ ).

The multiple concentration peaks noted in Fig. 4 and emphasized in Fig. 6 were unexpected. Could the multiple peaks be artifacts, related either to our analytical method or to splicing two cores to obtain a century-long record? Retrospective inspection of previous single-core data sets reveals that similar peaks indeed have been recorded, although at different relative amplitudes. Marcantonio et al. (2002, their Table 1) observed two Pb peaks in Core RD at dates similar to those found here (though their time resolution is poorer because they analyzed half as many 20th century samples). They place these peaks respectively near 55 cm depth (1983) and near 83 cm (1964). We also place the upper peak near 55 cm in Core RD, but insufficient deeper samples remained available to enable us to

look for the lower peak in this core. Instead, we found this peak at 17 cm in Core 55, also dated 1964.

Furthermore, the 1960s Cu and Zn peaks in Core 55 also were observed previously by independent optical spectroscopic methods (Cantillo et al., 1984; Helz et al., 1985b; Adelson et al., 2001). Favorable comparisons between Pb, Cu and Zn profiles in Fig. 4 and those of previous workers who analyzed these same cores oppose analytical artifacts as sources of the peaks.

Further south in Chesapeake Bay, in a core taken near the mouth of the Choptank, two peaks in the profiles of five elements, Co, Ni, Cu, Zn and Pb, have been observed (Owens and Cornwell, 1995). The peaks seem to be simultaneous for all five elements, similar to Fig. 6. Cadmium peaks at approximately 1980, 1960 and 1940 have been observed near the mouth of the Patuxent River by acid extraction/ICPMS (Zheng et al., 2003). Interestingly, the site that provided these data was too shallow to have been much exposed to water column anoxia; the core contained a negligible Mo anomaly, as would be expected in this circumstance.

These additional instances, in which multiple peaks were observed in single cores by analytical methods independent of ours, suggest that concentration peaks in chalcophile element profiles in Chesapeake Bay are real, are regional and require an explanation. Until now, these peaks have received little notice because most previous studies either involved insufficient numbers of samples to establish temporal trends clearly or insufficient numbers of elements to reveal the repeating pattern.

In the following sections, we examine hypotheses to explain chalcophile enrichments in Chesapeake Bay's sediments. If each element had independent sources with unique historic emission profiles, correlations among these elements would not be expected. Thus our goal is to identify the source of a dominant, multi-element anthropogenic

component that we infer from the evidence in Figs. 5 and 6 must control  $M_{\text{ex}}$  concentrations for all the correlated elements.

#### 4.1. Anoxia-controlled authigenesis

At the outset of this study, our favored hypothesis to explain the chalcophile element profiles invoked the trend toward more frequent and intense summertime anoxic events in Chesapeake Bay during the 20th century. However, association of chalcophile element peaks in Fig. 6 with discharge minima is opposite to expectation from this hypothesis. Anoxia is greatest in summers following high January–May river discharge (Hagy et al., 2004). Higher spring discharges deliver more plankton nutrients, promoting organic carbon fallout into the bottom water; they also sharpen vertical density gradients, suppressing bottom water ventilation. Both effects exacerbate summertime anoxia. In recent years, spring discharges have successfully predicted the intensity of hypoxia/anoxia during subsequent summers.

More generally, difficulties arise for any explanation of excess chalcophile elements in the RD/55 sediments based on the water column as the source. In Table 2, we show excess concentrations of the correlated elements averaged over the final decade's deposition at each site. Note that these concentrations are approximately equal at each site, despite the roughly 3-fold higher mass accumulation rate at the RD site. The simplest explanation for this agreement is that the  $M_{\text{ex}}$  concentrations are carried to deposition sites by the particles that are deposited. This would result in  $M_{\text{ex}}$  concentrations independent of mass accumulation rate, as observed. In the opposite limiting case, where depositing particles contain no  $M_{\text{ex}}$  and gain it subsequently by transfer from the water column, the higher deposition rate at RD might be expected to produce more dilute  $M_{\text{ex}}$  concentrations.

Additionally, in cases for which data are available, the water column contains insufficient dissolved concentrations of these elements to provide the sediments'  $M_{\text{ex}}$  concentrations. In the final three columns of Table 2, we compare annual  $M_{\text{ex}}$  accumulation in sediments with annual water column dissolved inventories. Annual inventories are clearly insufficient to explain annual  $M_{\text{ex}}$  accumulations at either site, even in the improbable event that the water column were 100% stripped of trace elements.

Previously published sediment profiles for  $\text{Mo}_{\text{ex}}$ , which does transfer from the water column to sediments in response to anoxia, differ from profiles of  $\text{Cu}_{\text{ex}}$  and other chalcophile elements (Adelson et al., 2001; Dolor et al., 2009). The key difference between the elements discussed in this paper and Mo is the latter's much larger concentration (0.11  $\mu\text{M}$ ) in seawater, which provides a robust Mo source for authigenic processes. The final row in Table 2 shows that the water column has ample capacity to supply the excess Mo found at these core sites. Dissolved Mo in the Bay is modestly, but measurable drawn down by authigenic Mo formation in the sediments (Scheiderich et al., 2010).

#### 4.2. Baltimore Harbor

Perhaps the most obvious hypothesis to explain chalcophile element enrichments posits that Baltimore Harbor sediment particles containing industrial contaminants are effusing into the Bay. A practical date for the industrial revolution on the Chesapeake is 1842, the year in which the westward-pushing Baltimore and Ohio Railroad reached the Appalachian coalfields. Baltimore, then the second largest city in the United States, was thus availed of an enormous fossil fuel supply. Possibilities swelled for steam powered industry and shipping as well as smelting and steel-making. The city's population ballooned five-fold in the remainder of the 19th century. At various times, Baltimore has exulted in possessing the largest copper smelter,

Table 2  
Comparison of  $M_{\text{ex}}$  accumulation fluxes with water column inventories.

	$M_{\text{ex}}$ core RD <sup>a</sup> ( $\mu\text{g/g}$ )	$M_{\text{ex}}$ core 55 <sup>a</sup> ( $\mu\text{g/g}$ )	Accumulation at RD <sup>b</sup> ( $\mu\text{g/cm}^2/\text{y}$ )	Accumulation at 55 <sup>b</sup> ( $\mu\text{g/cm}^2/\text{y}$ )	Water column inventory <sup>c</sup> ( $\mu\text{g/cm}^2/\text{y}$ )
Co	9.1	8.5	11	3.5	0.20
Cu	17	21.	20	8.7	2.5
Zn	125	117.	151	48	7.3
Ag	0.40	0.41	0.48	0.17	
Cd	0.59	0.55	0.71	0.23	0.34
In	0.035	0.046	0.042	0.019	
Sn	2.7	2.4	3.3	0.98	<2
Sb	0.52	0.57	0.63	0.23	
Te	0.065	0.070	0.079	0.029	
Tl	0.22	0.29	0.27	0.12	
Pb	35	30.	42	12	<1
Bi	0.11	0.13	0.13	0.053	
Mo	1.13	1.71	1.37	0.70	12

<sup>a</sup> Concentration averaged over final decade of deposition in each core.

<sup>b</sup> Flux obtained by multiplying concentrations by mass accumulation rates, i.e. 1.21  $\text{g/cm}^2/\text{y}$  for RD and 0.41  $\text{g/cm}^2/\text{y}$  for 55.

<sup>c</sup> Dissolved (0.45  $\mu\text{m}$  filter passing) amounts in 5 L of water based on Kingston et al. (1983; averages of stations 11-091, -092, -085, -086). The 25 m deep water column contains 2.5  $\text{L/cm}^2$  of water; estuarine circulation replenishes this water roughly twice per year. Thus trace element inventories in 5 L represent maximum trace element amounts that could be scavenged from the aqueous phase per year per  $\text{cm}^2$  of sediment. See Adelson et al. (2001) for more discussion of such estimates.

largest copper refiner and largest steel mill in the United States. In the 19th century it was the principal world supplier of chromium from mines in Maryland. It has been a prominent center of food canning (users of Zn, Sn and solder components), silverware fabrication, paint manufacture (users of pigments containing Cr, Co, Cu, Zn, Cd, As, and Pb) and countless other activities that could contaminate its environment with trace metals. Most of these activities have ceased in Baltimore in the decades since World War II. Nonetheless the sediments of its harbor retain a large legacy of trace element contaminants from its industrial past (Sinex and Helz, 1982; Mason et al., 2004).

One way to test Baltimore Harbor's possible role as a source is to determine if the  $M_{ex}/Zn_{ex}$  ratios in Harbor sediments match those in core RD/55. Unfortunately, data are available to make this comparison for only a few elements. Fig. 7 shows  $Cu_{ex}$  and  $Pb_{ex}$  plotted against  $Zn_{ex}$  in the Harbor's near-surface sediments (data from Baker et al., 1997). Like the Bay data in Fig. 5, the Harbor data align in ways suggestive of binary mixing of excess components with the lithogenic component. Individual tributaries to the Harbor have unique  $M_{ex}/Zn_{ex}$  signatures, but these are all different from corresponding signatures at the RD/55 sites (dashed lines). The implication is that the anthropogenic components in the Harbor and in the Bay are not the same. Additionally, the Harbor contains negligible  $Tl_{ex}$  (Dolor et al., 2009) and therefore could not serve as a source for this element in the Bay.

The difference between the anthropogenic components in the Harbor and the Bay is clearest in the case of  $Cu_{ex}$ . The data from Northwest Branch and Middle Branch (respectively, c and b in Fig. 1), where the copper smelter and refining plants were once located, fall along a trend in which  $Cu_{ex}/Zn_{ex} = 0.58 \pm 0.05$ . This markedly exceeds  $Cu_{ex}/Zn_{ex} = 0.147 \pm 0.007$  in the RD/55 data (Fig. 5). Curtis Bay (a) follows the same trend as Northwest and Middle Branches, but Bear Creek (d) follows a unique low-Cu/high-Zn trend ( $Cu_{ex}/Zn_{ex} = 0.087 \pm 0.004$ ), probably related to manufacture of galvanized iron and steel products in that area. An excess component having RD/55s  $Cu_{ex}/Zn_{ex}$  ratio could be fabricated by mixing 12% of the Northwest Branch sediments with 88% of the Bear Creek sedi-

ments, but it would be difficult to explain how material with just this mixing ratio could be supplied to RD/55 sites for decades. Similar difficulties confound any effort to link  $Pb_{ex}/Zn_{ex}$  ratios in the Bay to Baltimore Harbor sediments.

This analysis does not support Baltimore Harbor sediments as the dominant  $Cu_{ex}$  and  $Pb_{ex}$  source for the RD/55 sites, although the Harbor is not excluded as a minor contributor. It can be noted that Sinex and Helz (1982) concluded from independent arguments that the Harbor retains most of its contaminants. From their pollutant isopach map, they inferred that the known three-layer water circulation system in the Harbor must trap contaminated particles, resulting in their greatest accumulation farthest from the mouth.

The preceding arguments do not address the possibility that Baltimore Harbor sediments serve only as a reservoir of contaminants and that transfer of contaminants to Chesapeake Bay involves the aqueous phase. Riedel et al. (1999) estimate that Cd escaping from sediments could double the dissolved Cd concentration in water leaving the Harbor, while increasing the dissolved Cu concentration by about 40%. Thus, the ratios of these two elements in the water would differ from the ratios in the Harbor sediments. Nonetheless, the final column in Table 2 implies that measured dissolved concentrations of these elements in the Bay's water column, regardless of source, are inadequate to explain  $M_{ex}$  accumulations in the sediments.

### 4.3. Susquehanna Basin

In contrast to earlier hypotheses, the following lines of evidence support derivation of the Bay's chalcophile enrichment from the Susquehanna Basin. The Susquehanna River delivers 90% of the freshwater and most of the sediment entering northern Chesapeake Bay.

First, we can test whether the  $M_{ex}/Zn_{ex}$  signatures of the anthropogenic component in the Bay are similar to corresponding signatures from our three Conowingo reservoir samples. This test is done in Fig. 8, which summarizes the RD/55 data set in box plot format and compares these values with Conowingo mean  $M_{ex}/Zn_{ex}$  ratios, shown as star symbols. Except for  $Te_{ex}$  and  $Tl_{ex}$ , the Conowingo values

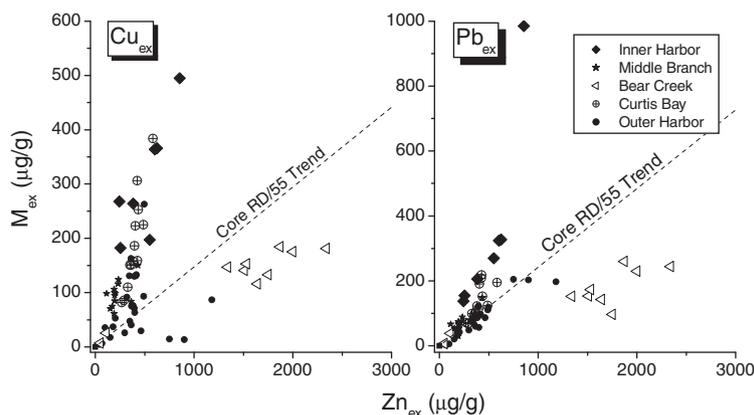


Fig. 7. Correlations of  $Cu_{ex}$  and  $Pb_{ex}$  with  $Zn_{ex}$  in Patapsco estuary (Baltimore Harbor). Data from (Baker et al., 1997). Lines are regression of Core RD/55 data from Fig. 5. Data for individual tributaries to the Patapsco are plotted separately (refer to Fig. 1 for locations of the tributaries).

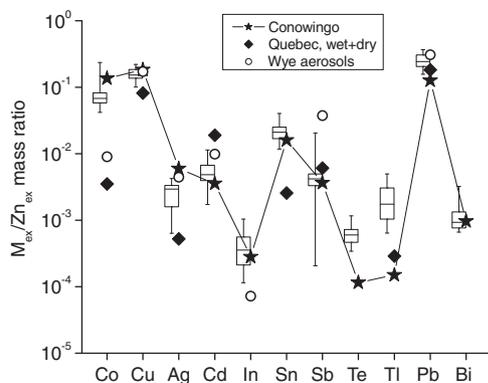


Fig. 8. Similarities in  $M_{ex}/Zn_{ex}$  among Chesapeake Bay sediments (boxes and whiskers), the mean of the Conowingo samples (star symbols connected by line segments), the sum of wet and dry atmospheric deposition in Quebec (diamond symbols; Gélinas and Schmit, 1998) and aerosols collected at Wye, MD (open circles; Wu, 1993). Elements are listed in atomic number order. The rectangular boxes enclose 50% of the data for each element in the core RD/55 data set. The horizontal lines dividing the boxes represent the medians, and the whiskers enclose the full range of the  $M_{ex}/Zn_{ex}$  data.

agree with the RD/55 medians to better than a factor of two. Apparently the anthropogenic components in sediments of the lower Susquehanna Basin and of Chesapeake Bay are very similar. For  $Te_{ex}$  and  $Tl_{ex}$ , additional sources in the Bay may be required. However, the disagreement also could be due to statistical variability owing to the small number of Conowingo samples as well as the analytical difficulty of determining these two least-abundant elements.

Second, fluvial erosion can account for the temporal relationship between trace element concentration minima and multi-year river discharge maxima shown in Fig. 6. High river discharge is known to scour stored sedimentary material from riverbanks and reservoirs in the lower Susquehanna Basin (Gross et al., 1978). It seems likely that much of this stored material has been sequestered for decades, or longer, and therefore largely has escaped anthropogenic contamination. During maximal discharge years, when scouring is greatest, the sequestered material will dilute anthropogenically contaminated material from the Basin's exposed soils. This variable dilution can explain why  $M_{ex}$  minima correspond to discharge maxima, and *vice versa* (Fig. 6). Independent evidence that higher Susquehanna discharges diminish total river-borne concentrations of certain chalcophile elements (Ni, Cu and Zn) relative to Fe has been presented previously (Helz and Sinex, 1986).

The roughly 20-year peak cycle identified in Fig. 6 is probably linked to a previously described 22-year regional hydrologic cycle (Yarnal and Leathers, 1988; Kirby et al., 2001). This latter cycle is recorded by a 1000-year oxygen isotope record in the sediments of Green Lake, located just to the north of the Susquehanna Basin. The cycle has been attributed to shifts in the winter position of the atmosphere's polar vortex (Kirby et al., 2001). Such shifts probably control how much Great Lakes moisture is deposited as snow in the Susquehanna Basin vs. in the St. Lawrence or Hudson Basins.

#### 4.4. Anthropogenic component's ultimate source

What human activities could be responsible for contamination at the scale of the Susquehanna Basin? Historically, this basin has been mostly devoid of industrial centers that could provide large point sources of trace element pollution. The industrial centers that surround the Susquehanna Basin (Buffalo, Pittsburgh, Baltimore, and Philadelphia) all lie in adjacent watersheds (Fig. 9).

Coal mining has been a widely distributed and economically important activity throughout the Susquehanna Basin for 150 years. Acid mine drainage from these operations is a potential source of chalcophile elements. Kairies et al. (2005) provide data from which we calculate  $Co_{ex}/Zn_{ex} = 0.22$ ,  $Ni_{ex}/Zn_{ex} = 0.25$ ,  $As_{ex}/Zn_{ex} = 7.6$  and  $Pb_{ex}/Zn_{ex} = 0.23$  in iron hydroxide precipitates from Pennsylvania and Maryland coal mine drainage. Except for  $As_{ex}/Zn_{ex}$ , which is very high, these values agree reasonably with corresponding ratios in Bay sediments (Figs. 5 and 8). Therefore mine drainage is a plausible contributor to the anthropogenic component in the Susquehanna Basin.

Nevertheless, the stable Pb isotope data of Marcantonio et al. (2002) are not consistent with derivation of  $Pb_{ex}$  in Chesapeake Bay cores dominantly from mine drainage. These workers find that  $^{206}Pb/^{207}Pb$  temporal variations

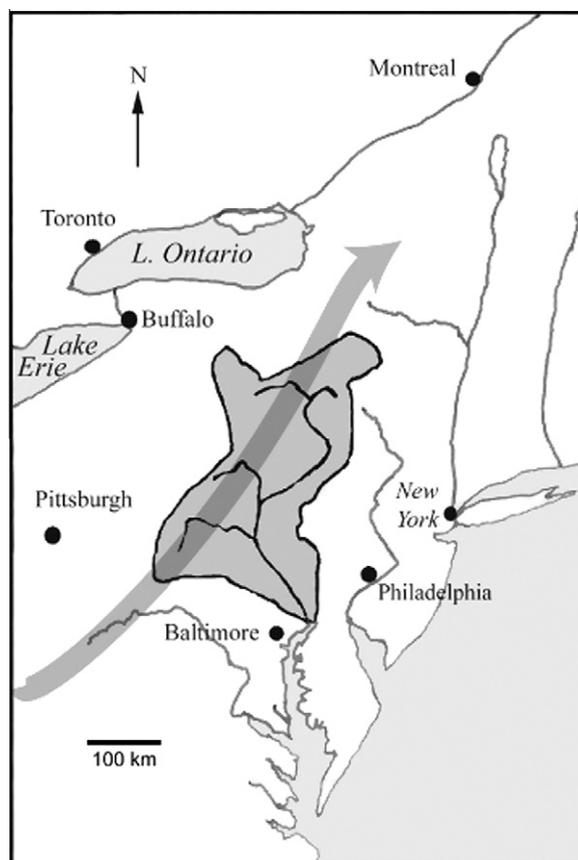


Fig. 9. Map of northeastern United States and southeastern Canada showing the location of the Susquehanna Basin. Arrow depicts the direction of transport of acid rain components from the United States' Midwest.

in Core RD track those in Bermuda corals. Both are assumed to track North American aerosols. Thus, if the excess trace element concentrations at Core RD/55 sites are imported from the Susquehanna Basin, as implied by Figs. 6 and 8, then aerosols, not mine drainage, must be the principal  $Pb_{ex}$  source in the Basin.

The Susquehanna Basin lies in the flow path of contaminated air originating in the Ohio River Valley and the southern Great Lakes regions – the industrial heartland of the United States (Fig. 9). Evidence for industrial contamination of air passing over the Susquehanna Basin can be found in data compiled by the National Atmospheric Deposition Program. In the early 1990s, before acid rain abatement measures took hold, rain in the Susquehanna Basin was near pH 4.2; sulfate, which is derived in large part from coal combustion, was being deposited in the Susquehanna Basin at rates that were among the highest in the United States (<https://nadp.isws.illinois.edu/>). Excess trace element concentrations have been deposited from the atmosphere onto remote watersheds for many hundreds of kilometers to the northeast of the Susquehanna Basin (e.g., Gélinas et al., 2000; Gallon et al., 2005; Laforte et al., 2005; Couture et al., 2008), and also must have been deposited within the Basin. Most of the elements discussed in this paper are subject to long-range atmospheric transport and are known to contaminate surface soils in remote forests (reviewed by Steinnes and Friedland, 2006).

Open circle symbols in Fig. 8 denote  $M_{ex}/Zn_{ex}$  ratios for seven elements in aerosols collected at Wye, Maryland (~20 km east of Core RD/55; Wu, 1993). Diamond symbols show eight  $M_{ex}/Zn_{ex}$  ratios in wet plus dry atmospheric deposition at rural sites in Quebec, about 800 km northeast of Chesapeake Bay (Gélinas and Schmit, 1998). The  $M_{ex}/Zn_{ex}$  abundances for both atmospheric data sets bear a resemblance to corresponding values for Chesapeake and Conowingo sediments. With the exception of  $Co_{ex}/Zn_{ex}$ , discrepancies are less than an order of magnitude and in fact are quite good in the cases of  $Cu_{ex}$  and  $Pb_{ex}$ . This general, but imperfect agreement between  $M_{ex}/Zn_{ex}$  ratios in atmosphere-derived materials and in Chesapeake Bay sediments points toward industrially contaminated air as a likely ultimate source for the excess chalcophile elements. Aerosol compositions almost certainly vary with date and location, so an imperfect agreement in these data sets may be the best that can be expected.

Although aerosol deposition might explain  $M_{ex}/Zn_{ex}$  signatures in Chesapeake Bay, we emphasize that direct transfer from the atmosphere to the Bay, without involvement of the Susquehanna Basin, is an insufficient source. This is true for most elements for which we have atmospheric deposition data, but is most easily illustrated with Pb. During the 1990s,  $Pb_{ex}$  was accumulating at the top of core RD at approximately  $42 \mu\text{g}/\text{cm}^2/\text{y}$  (Table 2). Owing to a  $^{210}\text{Pb}$ -based sediment focusing factor of ~6 at the site, obtaining this much excess Pb from the atmosphere would require a deposition flux to the water surface of  $7 \mu\text{g}/\text{cm}^2/\text{y}$ . During the same period, measurements of Pb deposition fluxes in precipitation at rural sites around northern Chesapeake Bay produced values of only about  $0.05 \mu\text{g}/\text{cm}^2/\text{y}$  (Mason et al., 2001). Total deposition from the atmosphere

(wet + dry) is estimated to be twice this, or  $0.1 \mu\text{g}/\text{cm}^2/\text{y}$  (Quinn and Ondov, 1998). Thus direct deposition is far too small to explain  $Pb_{ex}$  accumulations at core RD. The large multiplier effect that is created by the immense area of the Susquehanna Basin is necessary to reconcile aerosol deposition fluxes with sedimentation fluxes in the Bay.

It is interesting that the  $Ag_{ex}/Zn_{ex}$  ratio in Conowingo and Chesapeake sediments is similar to that in aerosols collected at Wye (Fig. 8), implying that the atmosphere could be the source of excess Ag. A decade ago, elevated Ag was regarded as a definitive marker of wastewater treatment plant outfalls (Sañudo-Wilhelmy and Flegal, 1992; Gobeil, 1999). However, more recent evidence suggests that aerosols can be an important anthropogenic Ag source at distances beyond the influence of individual wastewater treatment plants (Ranville and Flegal, 2005; Grahn et al., 2006). While we cannot exclude wastewater treatment plants in the Susquehanna Basin as the source of the Bay's Ag enrichment, the Wye aerosol data show that treatment plants' involvement is not proven by Ag enrichment.

The 1920–1940 timing of the rise in chalcophile element concentrations is compatible with their derivation from regional aerosols. Coal combustion, a major source of trace metal-contaminated aerosols, rose fairly steadily in the United States between 1880 and 1920 and then leveled off for 50 years before rising again (Shen and Boyle, 1987). Growth of a chalcophile signal in Chesapeake Bay would be expected to lag growth in coal combustion if these elements had to build up on soils of the Susquehanna Basin before the signal could be transmitted to the Bay. Accumulation of chalcophile elements on soil particles, followed by mixing during erosion and transport to the Bay is an appealing mechanism for generating a homogeneous anthropogenic component. If this view is correct, then it would be difficult for Society to reduce concentrations of chalcophile element contaminants in Chesapeake Bay and similar estuaries. The contaminants already reside in the source region in a highly dispersed form.

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